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Silica sols as refractory fibre binders

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Abstract

Four different colloidal silica sols with different specific surface areas (from 80 up to 360 m^2/g) and particle sizes have been examined in an application as refractory fibre binders. The fibrous materials were fabricated using a vacuum-forming technique, and a cationic starch was used as flocculent to obtain high retention of silica. The starch molecule also works as a temporary binder in the fibre product. Optimum retention and, hence, the most homogeneous fibre bodies were obtained at a constant ratio between the starch addition and the total surface area of the added silica, regardless of the type of silica sol used. The compressive strength of the fibre products depended mainly on the density of the fibrous materials. The density increased with increased starch content. The green strength was higher than the strength of the sintered samples, as starch is an effective binder. The sol with the best overall properties had a particle size of about 15 nm and an intermediate specific surface area (220 m^2/g). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceramic fibres can be shaped to simple components using several different techniques. A useful technique for the forming of a fibrous material of high-volume fraction fibres involves the preparation of a slurry of short fibres in a liquid, usually an aqueous medium, and letting the liquid drain from the slurry in a mould. The drainage of liquid may be assisted by high pressure or vacuum. The refractory fibres are usually bound together by an inorganic binder (consisting of, for instance, soluble alkali silicate, ethyl silicates, phosphates or colloidal silica). These fibrous materials will have high porosity, which gives them low density and low thermal conductivity. The combination of very good thermal shock resistance and low thermal expansion makes these fibrous materials suitable in thermal insulation of, for instance, furnaces, heating jackets, combustion chambers or space shuttles.[1–3] Other applications for these fibrous materials are as ceramic preforms when producing metal–matrix composites (MMC) through squeeze casting or liquid metal infiltration.[4–6] Only when the preform has sufficient strength will it resist cracking or deformation during squeeze casting and metal infiltration.

The choice of binder system is very important for the final properties of the fibrous products. To obtain the most homogeneous fibre product, the binder should be bonded or adsorbed to the fibres. If the binder is not adsorbed, it will migrate during the forming stage, resulting in an uneven distribution of the binder and a fibre product with a hard shell and a soft centre. Colloidal silica is today the most frequently used refractory binder for ceramic fibres and there are many types of silica sols commercially available.[7] Colloidal silica sols consist of extremely small, non-porous amorphous particles in water. The nanosized particles are stabilised by a small amount of alkali, often sodium. The chemistry of silica sols has been thoroughly described by Iler.[8] However, in order to obtain high retention of silica (negatively charged) to the ceramic fibres (negatively charged), a positively charged polyelectrolyte is often used to achieve the desired flocculation. An often-used polyelectrolyte is *cationic starch* owing to its effective flocculation properties.

Starch is a complex polymer because it consists of a mixture of two polysaccharide types (amylose and

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amylopectin) and both are polydisperse.[9] Amylose is a linear polymer, whereas amylopectin is highly branched, see Fig. 1a and b. Amylopectin, which is an excellent flocculating agent, is usually the dominant component in the starch granule. According to the literature,[9,10] the amylopectin molecule is one of the largest natural polymers known, with molecular weights of 10^7–10^9 g/mol and a hydrodynamic radius of at least 100 nm. It should be emphasised that the amylopectin molecule is much larger than the colloidal silica sol particles. The starch molecules will be adsorbed to both the small silica particles and the long fibres by electrostatic forces, and loosely bound flocs are formed, see the schematic drawing in Fig. 2. This flocculation increases the rate of the dewatering process. High retention of silica, starch and fibres is very positive because these processes are usually run in closed systems. It should be noted that both the starch and the silica sol have double functions. They are components in the retention system, besides being very effective binders. The starch molecules give high (green) strength to the product up to about 250°C (at about 300°C the starch is burnt out) and the silica binder acts as a high-temperature binder (after firing at about 1000°C). The silica binder gains its binding power through the coalescence of the silica particles on the loss of water. The green strength is very important because most refractory fibrous products are installed in the furnaces *before* firing. The green strength, therefore, determines how the material resists handling, transportation and installation. After firing at 1000°C, the silica gel crystallises to cristobalite. The crystallisation temperature and the rate of crystallisation depend on the alkali content in the silica sol.[7,11] The fibrous material should obtain full strength after firing at 1000°C.

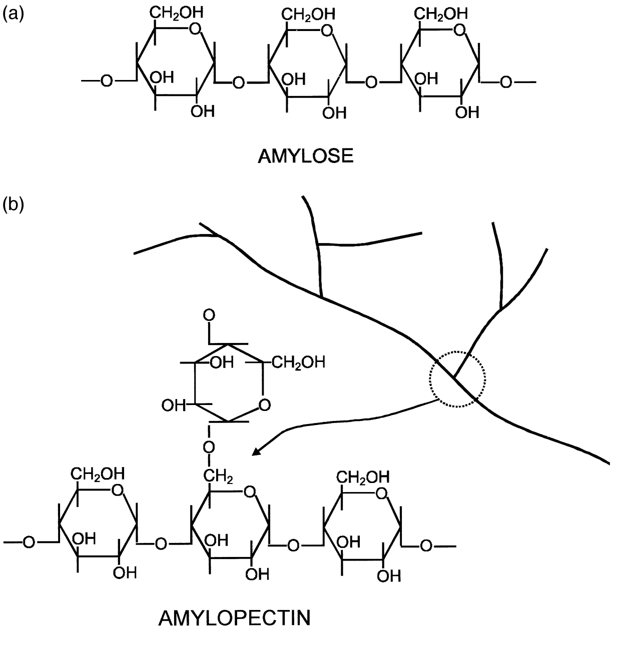

Fig. 1. Chain of glucose forming the amylose (a) and the branched structure of amylopectin (b) (from Ref. 9).

Except for some patents[5,6,12,13] very few studies are published in the field of processing and characterisation of ceramic fibrous products and preforms. Exceptions are the thorough studies performed by Chiou and Chung.[14–17] They mainly studied the effect of different Al-phosphate binders in the fabrication of ceramic fibre preforms. As a reference, preforms with colloidal silica were prepared, but in this case no cationic polyelectrolyte was added to obtain flocculation of the fibres and the silica binder. Therefore, no strong binding of silica to the fibres was achieved and hence, an inhomogeneous distribution of the binder was obtained. An inhomogeneous distribution of the silica binder was probably also the reason for the very low mechanical strength of fibrous preforms with silica binders reported by Crankshaw and Clegg.[18]

The particular retention system, consisting of colloidal silica sol and cationic starch, also named "microparticulate system" (although the sol consists of nanoparticles) is widely used in the fabrication of paper, and many similarities can be seen in this kind of process and the one described above. The high speed of modern paper machines has increased the demand for efficient flocculent systems. The flocculation behaviour of the microparticulate system consisting of silica sol, cationic starch and cellulose fibres has been thoroughly studied in a number of scientific papers.[19–21] Some papers have focussed on the adsorption behaviour of the cationic potato starch onto microcrystalline cellulose or cellulose fibres,[22,23] whereas Wall et al.[24] and Larsson and Wall[25] concentrated their more fundamental studies on a system consisting of only silica sol and cationic starch. From studies on the heteroflocculation of this microparticle system, it was concluded that the electrostatic

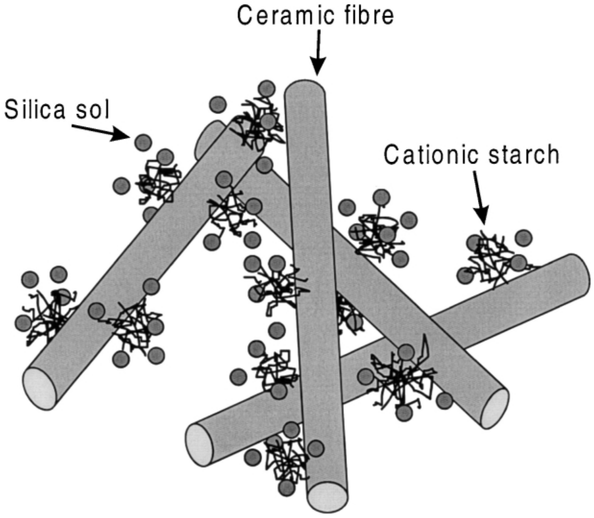

Fig. 2. Schematic figure of the flocculation of the negatively charged fibres and negatively charged silica sols with cationic starch.

forces were very important, and maximum flocculation was found when the two polyions contributed to the same amount of charge. Therefore, it has been suggested that the most important mechanisms of microparticle systems should be electrostatic interaction and bridging.[21] The silica particle acts as a bridge in the formed floc.

The aim of this study was to gain a deeper understanding of this three-component system — consisting of ceramic fibre, silica sol and cationic starch — to optimise the process and the final fibre product. Four different types of colloidal silica sols were evaluated in the study.

2. Experimental

2.1. Material

2.1.1. Ceramic fibre

The fibre used was an alumino-silicate fibre, Fiberfrax CEF 103 from Carborundum Resistant Materials, England. The fibres consist of 53 wt.% SiO_2 and 47 wt.% Al_2O_3. The lengths of the fibres were 0.5–10 mm and their diameter was around 2 μm. The isoelectric point was at pH 3.5, which means that the fibres will be negatively charged in the slurry (which has pH 9). The melting temperature of this fibre is, according to the producer, 1760°C. The Fiberfrax fibres also contain a fraction, ~50 wt.%, of non-fibrous materials, so called shots (d~180 μm).

2.1.2. Silica sol

Four different commercial colloidal silica sols, produced by Eka Chemicals AB (Bohus, Sweden), were evaluated in the study. The different sols and selected properties are presented in Table 1. All sols had negatively charged particles, but the specific surface areas and particle sizes varied between the sols, from 80 m^2/g ($d_p \sim 40$ nm) up to 360 m^2/g ($d_p \sim 9$ nm).

2.1.3. Cationic starch

The same cationic starch, Solvitose N (produced by AVEBE, Holland) was used in all the experiments. Solvitose N is a potato starch, modified with quaternary ammonium groups to make it keep a positive charge in a wide pH range. The nitrogen content was 0.22 wt.% and the degree of substitution, D.S., was 0.028–0.032 mol/mol (according to the manufacturer). This means that about 3% of the hydroxyl groups had been substituted to ammonium groups to change the polarity of the starch.

Solvitose N is a cold-swelling type of starch and this type is easy to use. Before use, the starch was dissolved in water at room temperature by stirring. The concentration of the starch suspension was <3 wt.%.

2.2. Fabrication of the fibrous materials

All experiments were conducted in the same manner. The fibres were initially dispersed in tap water by high-speed stirring and the predetermined amount of silica sol was added. The highly charged silica sol particles have a dispersing effect on the fibres and this enhances the preparation of a homogeneous fibre suspension. Different amounts of starch (predissolved in water) were finally added to the fibre–sol suspension to find the optimum amount of starch for each silica concentration, i.e. the amount of starch that gave the most effective retention of silica and starch. Since the starch molecules have a positive charge, they flocculate the negatively charged fibres and silica particles. This preparation procedure was chosen, because a separate study had shown that this order of addition of the different components gave the best retention of starch and silica. Addition of starch before the silica addition did not give the same good flocculation behaviour.

Tap water (ionic strength: 2.2 mM, conductivity: 23.8 mS/m) was used in all experiments in this study, but in some cases additional experiments with different ionic strengths were made to examine the importance of the process water used.

The types of sols and the silica concentrations used in the experiments are summarised in Table 2. The amount of ceramic fibre was 100 g in all experiments. For comparison between the different sols either the weight of silica (4 g) or the total surface area of silica (880 m^2) was kept constant. The concentration of fibres in the final suspension was about 5 wt.% (1.8 vol%). The final suspension contained about 0.1–0.5 wt.% silica and

Table 1
Properties of colloidal silica sols

Grade	SiO_2 (wt.%)	Na_2O (wt.%)	pH	Specific surface area (m^2/g)	Particle size (nm)
Bindzil 50/80	50	0.22	9.3	80	40[a]
Bindzil 40/130	40	0.18	9.0	130	25
Bindzil 40/220	40	0.40	9.7	220	15
Bindzil 30/360	30	0.55	10.0	360	9

[a] Wide particle size distribution.

Table 2
Type of silica sol and concentration of silica used

Type of silica sol	Amount of silica (g)[a]
Bindzil 50/80	4, 8 and 11 (=880 m^2)
Bindzil 40/130	4 and 6.77 (=880 m^2)
Bindzil 40/220	4 (=880 m^2)
Bindzil 30/360	2.44 (=880 m^2) and 4

[a] Each system contains 100 g of ceramic fibre.

0.02–0.35 wt.% cationic starch based on the total weight of the slurry. The pH of the suspension was about 9.

The fibrous materials were fabricated using a vacuum-forming technique. The fibre–sol–starch slurry was poured into the cylinder tank of the vacuum-forming equipment and the water was drained off using vacuum. A 50 μm filter was placed at the bottom of the tank to hinder the fine fibres from disappearing together with the filtrate. The same weight (5 kg) was placed on top of the slurry in all experiments to compress the fibre body during the vacuum forming. Fibrous plates with a cylindrical shape were formed ($d \sim 100$ mm, $h \sim 20$–35 mm). The effluents obtained from the vacuum forming of each sample were collected for further analysis.

The fibre materials were first dried at room temperature and then at 110°C until a constant weight was reached. Four cylinders ($d \approx 35$ mm) were drilled out from each of these dried plates. Two of the samples were tested directly, whereas the other two were sintered at 1000°C for 90 min (5°C/min).

2.3. Analysis and mechanical evaluation

The turbidity of the effluent gave a first indication of the retention of starch and silica in the system. A clear effluent meant that almost all silica and starch were retained in the fibre body after the vacuum forming. The turbidity was analysed by a turbidiometer (HACH 18900).

The concentrations of silicon and carbon in the effluent were also analysed (by Eka Chemicals AB), which gave a more accurate result of the amount of silica and starch retained in the fibre body. The content of silicon was analysed using an ICP method (inductive couple plasma) and the starch content was obtained by analysing the total organic content (TOC) in the sample.

The density of the samples before sintering was determined by measurement of the dimensions of the dried fibre cakes, whereas the density of the sintered samples was determined mainly by a water intrusion method according to Archimedes' principle (EN6232: 1993).

The mechanical testing of all samples was conducted using a universal testing machine, type Zwick 1464 of Zwick GmbH. The crosshead speed used was 1.27 mm/min for each 25 mm thickness, which is in accordance with the American ASTM C 165-95 standard. The direction of the compression was parallel to the direction of the vacuum forming. The samples were compressed by 20% linearly. The elastic strength (σ_e) at the yield point and the strength for 10% deformation were taken (σ_{10}).

Scanning electron microscopy (JEOL-5300) was used to observe the location and appearance of the silica binder in the sintered fibrous structures. Fracture surfaces parallel to the direction of the vacuum forming were studied. The fibrous materials were coated with gold before the analysis.

3. Results

3.1. Turbidity and retention

All experiments gave similar results, i.e. maximum retention of silica and starch was obtained when a certain amount of starch was added (Table 3). As an example, the results from the turbidity measurements and chemical analyses with Bindzil 40/220 are seen in Fig. 3. In the region of optimum retention, the chemical analyses showed that the retention of silica and starch was very high and the turbidity was very low (<5 NTU). Table 4 shows that the retention of silica and starch was high ($>94\%$) for all tested systems. However, the results also indicate that the retention of silica was highest for the sol with the lowest specific surface area (i.e. Bindzil 50/80). In this case $>99\%$ of the added silica was retained. The retention of silica slightly decreased with an increase in the specific surface area of the sol.

The results from the flocculation studies with the sols with the same total surface area of silica (880 m^2) are summarised in Fig. 4. As can be seen from Fig. 4 and Table 3 (see the overlapping intervals in column 3 for systems with 880 m^2 SiO_2 added) the regimes for optimum retention were obtained in nearly the same interval, 2.7–3.5 g starch, for all four sols. The overlap of the different curves in Fig. 4 would have been even better if more data points had been taken for the Bindzil 30/360 and Bindzil 50/80 systems.

If the amount of starch added is instead correlated to the total surface area of silica, it can be seen that optimum retention was gained in the interval of 3.5–3.8 mg starch/m^2 silica surface area, regardless of the type of sol and the amount of sol added (see the overlapping intervals in column 4, Table 3). This means that the optimum amount of starch to add to reach optimum retention would be about 3.65 mg starch/m^2 silica (average value taken from the interval of 3.5–3.8 mg starch/m^2 silica), if we were to test a new type of silica

Table 3
Amount of starch needed to obtain optimum retention

Type of silica sol	Amount[a] of silica (g)	Optimum retention[b] Amount[a] of starch (g)	Optimum retention[b] Amount of starch/ total silica surf. area (mg/m^2)
Bindzil 50/80	4.0	0.6–1.2	1.9–3.8
	8.0	1.5–2.5	2.3–3.9
	11.0 (880 m^2)	2.1–3.5	2.4–4.0
Bindzil 40/130	4.0	1.4–2.3	2.9–4.4
	6.77 (880 m^2)	2.6–3.8	3.0–4.3
Bindzil 40/220	4.0 (880 m^2)	2.6–4.6	3.0–5.2
Bindzil 30/360	2.44 (880 m^2)	2.7–4.0	3.1–4.5
	4.0	5.1–7.0	3.5–5.0

[a] The amount of silica and starch added is for a system with 100 g of ceramic fibre.

[b] "Optimum retention regime" defined for the regime (amount of starch added) which has given turbidity values < 5 NTU.

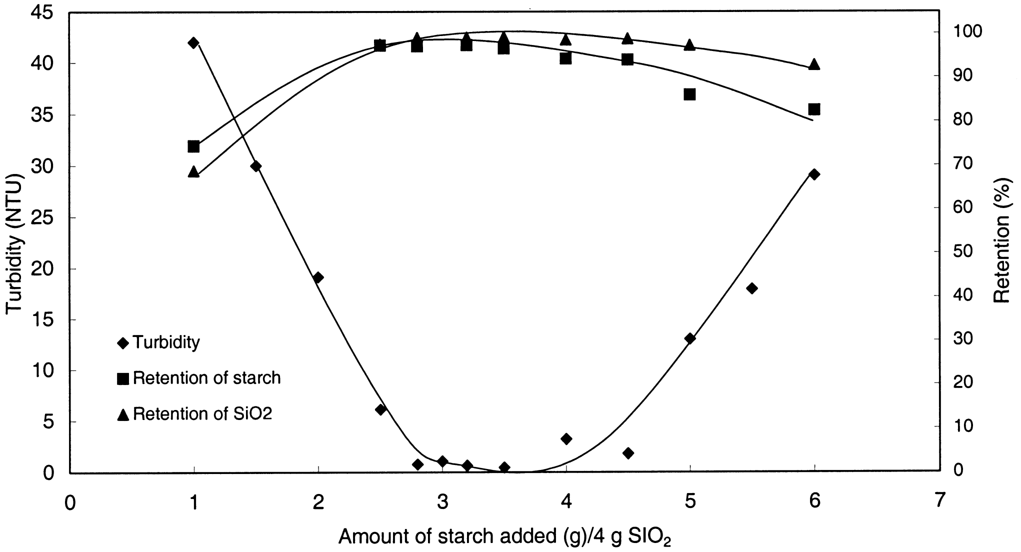

Fig. 3. Turbidity of the effluent and retention of starch and silica in the fibre products with Bindzil 40/220 added as binder (4 g SiO_2).

Table 4
Amount of silica and starch retained in the optimum retention regime

Type of silica sol	Amount[a] of silica (g)	Optimum retention[b] of silica (%)	Optimum retention[b] of starch (%)
Bindzil 50/80	4.0	>99	96.5–98
	8.0	>99	98.5–99
	11.0 (880 m^2)	>99	~99
Bindzil 40/130	4.0	~98.5	97.5–99
	6.77 (880 m^2)	98.5–99	98–99
Bindzil 40/220	4.0 (880 m^2)	97.5–99	94–97.5
Bindzil 30/360	2.44 (880 m^2)	94–96	94–98
	4.0	94.5–96	96.5–98

[a] The amount of silica and starch added is for a system with 100 g of ceramic fibre.

[b] Amount of silica and starch retained in the optimum retention regime (with turbidity of < 5 NTU).

sol. It has to be borne in mind that this amount of starch is correct only for this particular type of starch, Solvitose N. Other types of starches with other degrees of substitutions (other D.S. values) would give other values.

The flocculation behaviour very much depends on the ionic strength and the results hitherto discussed have been for systems with constant ionic strength (2.2 mM). The importance of the ionic strength was examined in a separate study, the results of which are presented in Fig. 5. More starch was required to obtain maximum retention at low ionic strength, but an increase in ionic strength (as + 5 mM $CaCl_2$ to tap water) gave optimum retention with a smaller amount of starch added. The reason for this is that the ionic strength strongly affected the configuration of the polyelectrolyte (cationic starch), and thereby also the flocculation and the adsorption behaviour of the starch molecule.[23,25] When you have low ionic strength, the starch molecule has a linear configuration owing to the repulsion of the charged

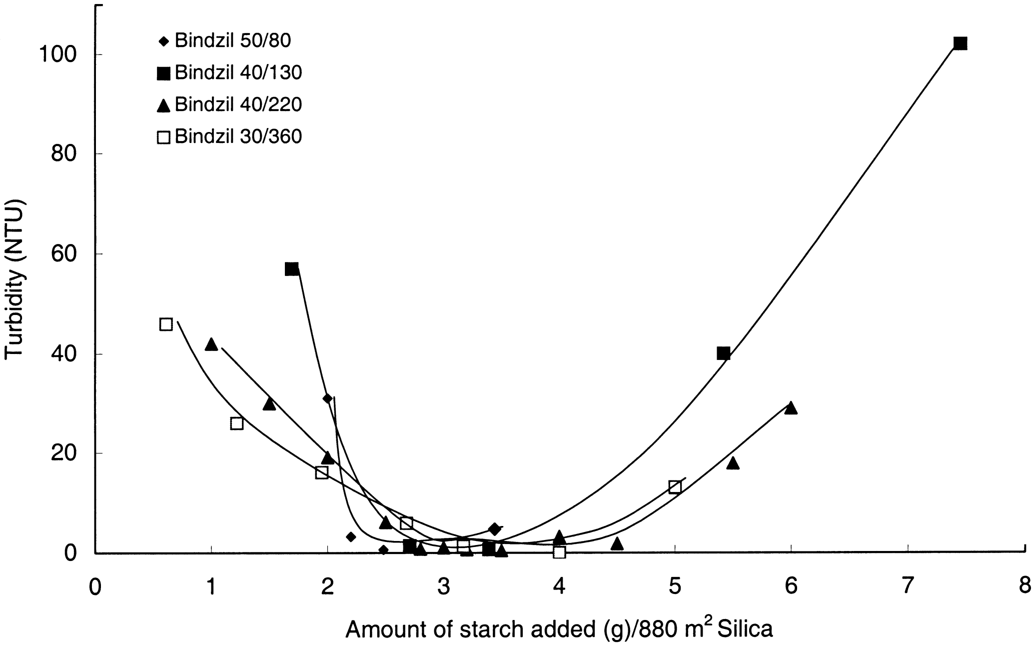

Fig. 4. Turbidity of effluents vs amount of starch added for all tested silica sols (880 m^2 silica added).

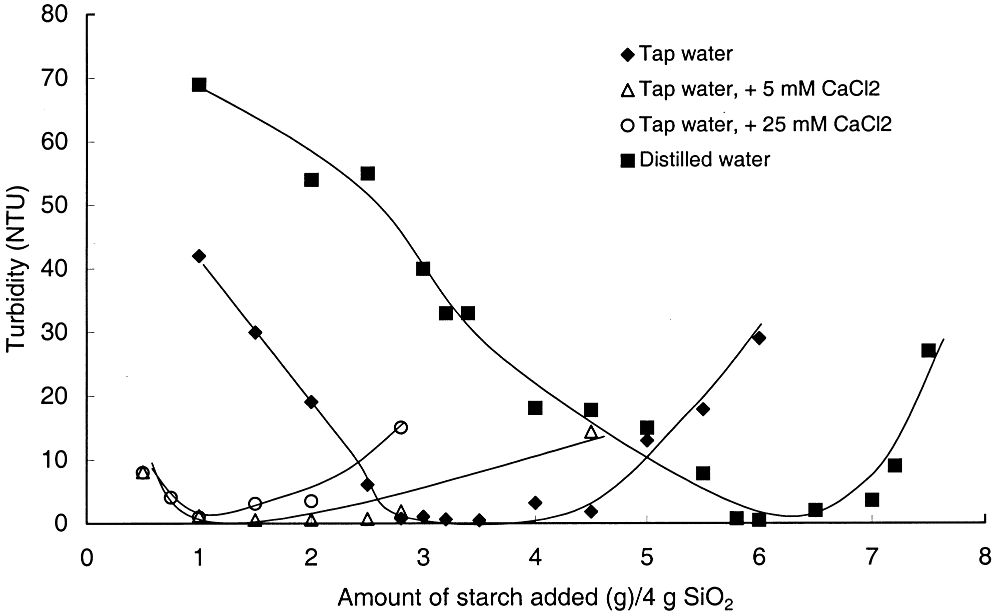

Fig. 5. Turbidity of the effluents in systems with different ionic strength. Bindzil 40/220 (4 g silica) added as binder.

groups. At high ionic strength the electrostatic forces are screened by counter ions and the starch molecule has a more coiled structure. The electrolyte also screens the charged fibres and the silica particles, which means that the adsorption behaviour of the starch molecules is affected. The results presented in Fig. 5 are also in accordance with earlier results presented by Larsson and Wall,[25] who studied the flocculation behaviour of cationic starch and colloidal silica under varied salt conditions. They showed that salt decreases the interaction distance of electrostatic forces between the silica particles and the starch molecules, which means that the demand for charge neutrality decreases and the flocculation interval increases.

3.2. Density

The results show that the difference in density values between the green samples and the sintered ones was rather small. The density of the fibre cakes very much depends on the amount of starch added, see Figs. 6 and 7. These figures show the density of the sintered fibre cakes made with either the same weight of silica (Fig. 6) or the same total area of silica added (Fig. 7). It is

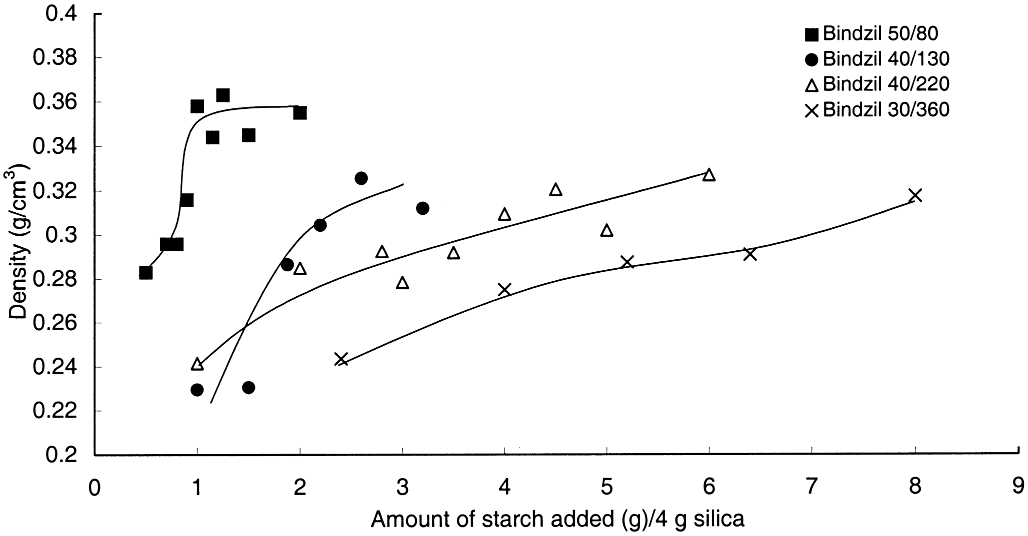

Fig. 6. Density of sintered fibre products with different silica sols (4 g SiO_2 added).

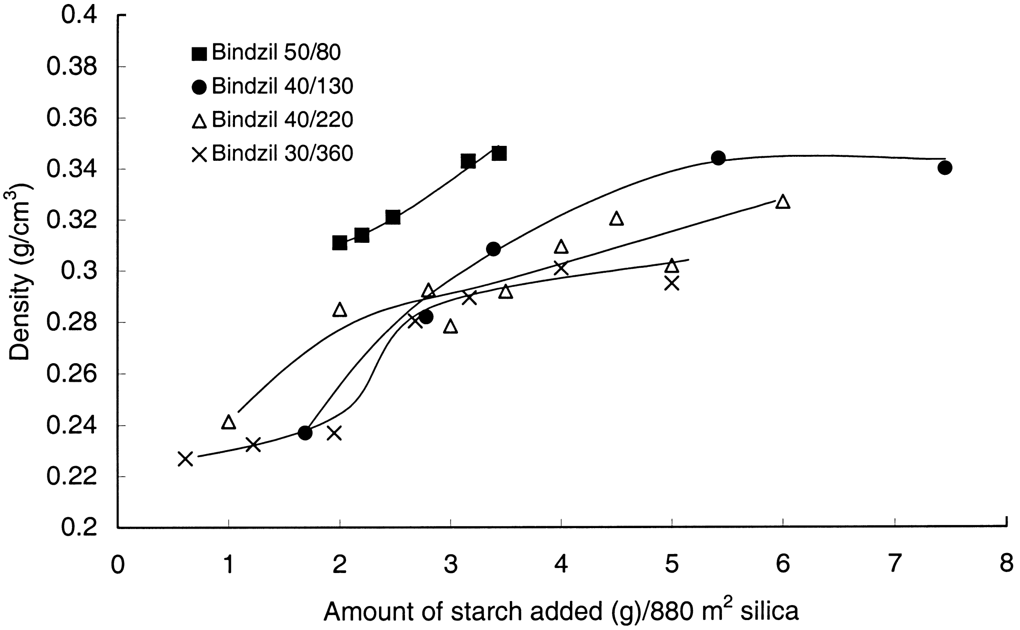

Fig. 7. Density of sintered fibre products with different silica sols (880 m^2 SiO_2 added).

clearly seen that the density increased with an increase in the amount of starch added. The increase was larger than what could be explained by the increased amount of starch added. The results indicate that the starch addition influenced the fibre rearrangement during the dewatering process and that the starch molecules tended to act as a lubricant for the fibres.

Fig. 7 shows that the density values were in the same range for most of the sols made with the same total area of silica and the same amount of starch added. The exceptions were the samples containing Bindzil 50/80, which had higher density. However, it has to be noted that, in this case, a very large amount of silica was required to reach 880 m^2 (11 g). This means that an excess of silica was added.

3.3. *Compressive strength*

Although the elastic strength was determined, only the values of the compressive strength for 10% deformation will be presented in this paper. As the binder is weak compared to the ceramic fibres under compression, the sample fails at the binder rather than at the fibres.

The compressive strength for 10% deformation of fibre materials with either 4 g or 880 m^2 silica, *before* ("green", dried at 110°C) and *after* sintering (at 1000°C) is illustrated in Figs. 8 and 9. The results show that the compressive strength increased with increased amounts of starch added. The results also show that in general the compressive strength was higher for the green samples than for the sintered ones. This is due to the very effective role of the starch molecules as a binder. After sintering, when the organic starch binder had been burned out, the strength of the fibrous structures decreased dramatically. However, for the colloidal sols with the lower specific surface areas (Bindzil 40/130 and Bindzil 50/80), the values of the green and the sintered samples were at about the same level, especially in those cases when small amounts of starch were added.

Since the amount of starch is very important for the green strength, it is interesting to compare the different sols under these circumstances when the same amount of starch was used, see Fig. 9. When studying the results in the optimum regime (2.7–3.5 g starch added), it can be seen that the fibre products with Bindzil 50/80 and Bindzil 40/220 had the highest green strength. Bindzil 50/80 also gave the highest sintered strength. The sintered strengths of the fibre bodies with the other three sols were at nearly the same, relatively low level. The results in Fig. 9 indicate that the silica sol with the highest specific surface area (Bindzil 30/360) gave the lowest strength of both green samples and sintered samples.

The results in Figs. 8 and 9 will be further evaluated to get a better understanding of the system. A few selected samples prepared with Bindzil 40/220 were studied regarding their composition, density and mechanical properties and the results are presented in Table 5. All these samples were prepared with 4 g SiO$_2$ (880 m^2 silica), but with different amounts of starch: an insufficient amount of starch (1 g), optimum amount of starch (3.5 g) and an excess of starch (6 g). It can be expected that the presence of silica is not critical for the green strength. Table 5 shows that the green strength strongly

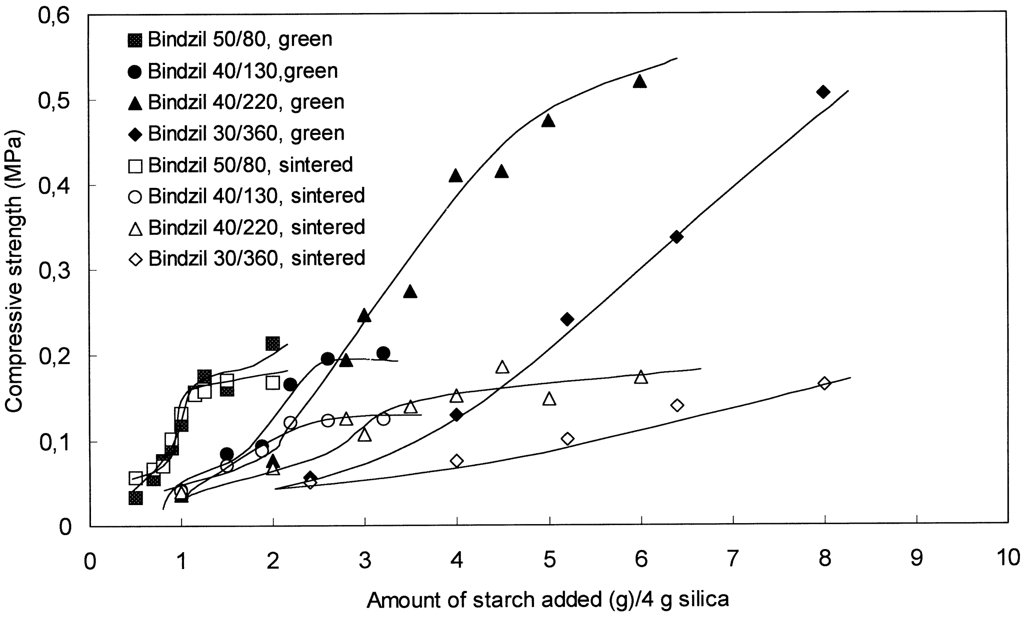

Fig. 8. Compressive strength (σ_{10}) for green and sintered fibre products with different silica sols (4 g SiO$_2$).

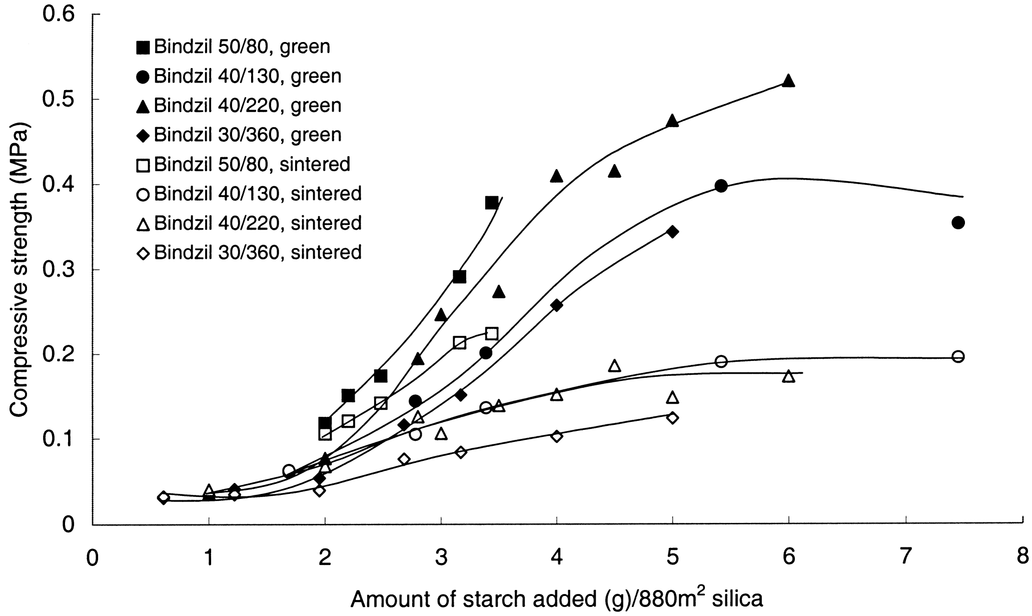

Fig. 9. Compressive strength (σ_{10}) for green and sintered fibre products with different silica sols (880 m^2 SiO$_2$). Optimum retention for the addition of 2.7–3.5 g starch.

Table 5
Properties of selected samples prepared with the Bindzil 40/220 sol and 100 g ceramic fibre

Preparation of samples		Properties of green samples			Properties of sintered samples		
Amount of silica added (g)	Amount of starch added (g)	Amount of starch in dried sample (g)	Green density (g/cm^3)	Green strength (MPa)	Amount of silica in sintered sample (g)	Sintered density (g/cm^3)	Sintered strength (MPa)
4	1	0.75	0.24	0.04	2.75	0.24	0.04
4	3.5 (Optimal amount)	3.38	0.29	0.27	3.97	0.29	0.14
4	6	4.95	0.33	0.52	3.71	0.33	0.17

increased with an increased amount of starch added. It should be emphasised that the green strength also increased when an excess of starch was added outside the region of maximum retention. There are two reasons for this behaviour. First of all, the amount of starch retained in the sample increased up to 4.95 g starch when 6 g starch was added. Furthermore, the density of the samples increased with an increased amount of starch added.

It is interesting to note that the sintered sample with the largest amount of silica retained did not have the highest strength. The sintered strength continued to increase also outside the region for optimal retention. However, this increase was not as pronounced as was the case of the green samples. The reason for the increase in strength was that the density of the sintered samples increased with increased amounts of starch added during preparation. It has earlier been shown (Figs. 6 and 7) that the density increased for all systems with increased amounts of starch added.

The results indicate that the green strength was affected by *both* the starch content and the density, whereas the sintered strength was more strongly correlated to the density value than to the silica content. Even if these results were obtained for the systems to which Bindzil 40/220 was added, similar results were achieved with the other types of sols.

Owing to the importance of the density, the compressive strengths of the samples must also be presented as a function of the densities of the fibre cakes (Figs. 10 and 11). The figures show that the compressive strength was nearly constant at low densities, <0.27 g/cm^3 (small amount of starch added), regardless of sol type and whether the material was sintered or not. For materials with high densities, >0.27 g/cm^3, the sols with the higher specific surface areas in general gave higher strength. This was most pronounced for the green samples.

Regardless whether the sols with the same amount of silica or the same total surface area of silica are compared, Bindzil 40/220 gave slightly higher compressive

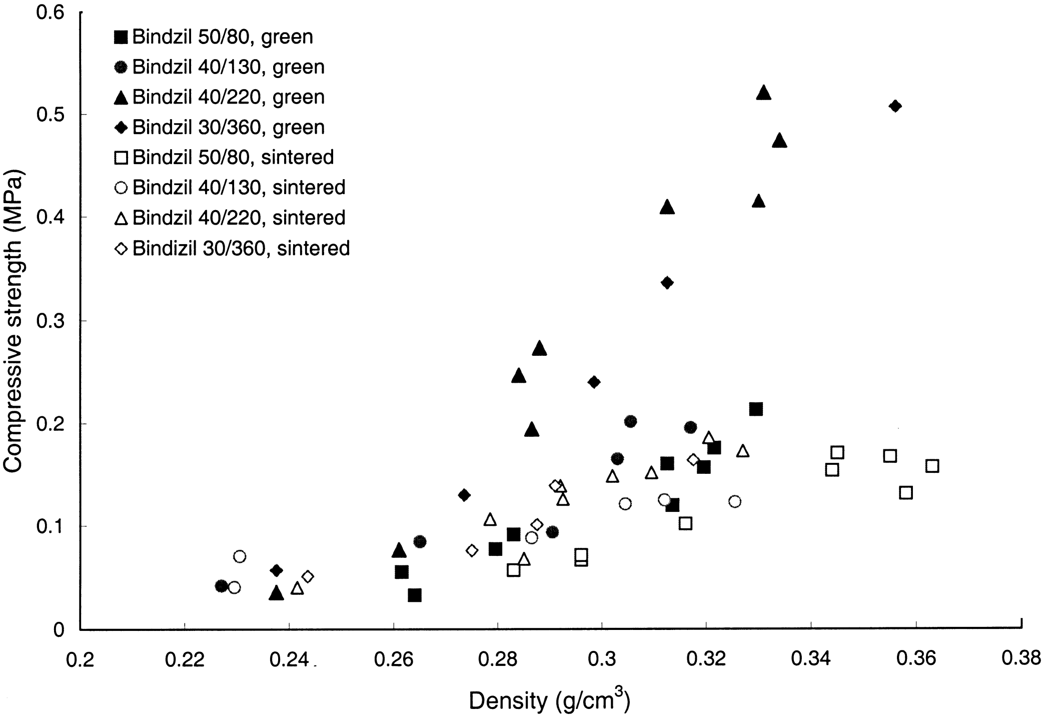

Fig. 10. Compressive strength (σ_{10}) vs density for green and sintered fibre products with different silica sols (4 g SiO_2).

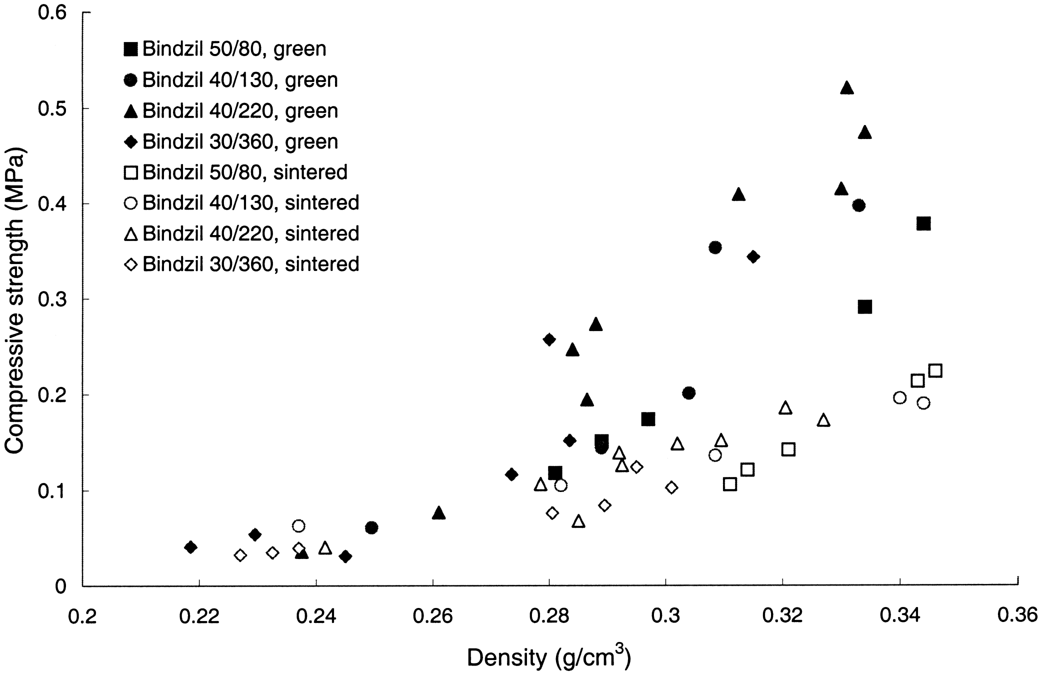

Fig. 11. Compressive strength (σ_{10}) vs density of green and sintered fibre products with different silica sols (880 m^2 SiO_2).

strength than the other sols (see Figs. 10 and 11). The sol with the lowest specific surface area, Bindzil 50/80, gave the lowest strength when the density had been taken into consideration.

3.4. Microstructure

The microstructures of some selected materials (after sintering) with Bindzil 50/80 or Bindzil 40/220 added as silica binder are seen in Figs. 12 and 13. One difficulty when studying these fibrous samples is the tendency of the samples to be charged up.

In these micrographs it is seen that even in the optimum retention regime (Figs. 12a and b, 13b), the silica gel is found not only in the contact points between the fibres, but above all it is located in the spaces between the fibres and, in most cases, the silica is also coating the fibres. Even with relatively small amounts of silica (such as 4 g silica from Bindzil 50/80) it can be seen that the silica gel is surrounding the fibres (Fig. 12a).

According to the micrographs, the silica gel in the sintered materials had most cracks when the sol Bindzil 40/220 sol was used (Fig. 13 b). Only a few cracks were seen in the gel made of Bindzil 40/130 and Bindzil 30/360. Fewer cracks were seen in the samples made of the sol with the lowest specific surface area, Bindzil 50/80 (80 m^2/g) (Fig. 12a and b). One explanation to this could be that Bindzil 50/80 consists of particles with a wide size distribution enhanced the packing of the sol particles and that this led to a relatively dense gel.[7] It can be expected that the shrinkage of this kind of gel would be smaller than that of gels from the other sols, and, hence, the gel would be less crack-sensitive. The

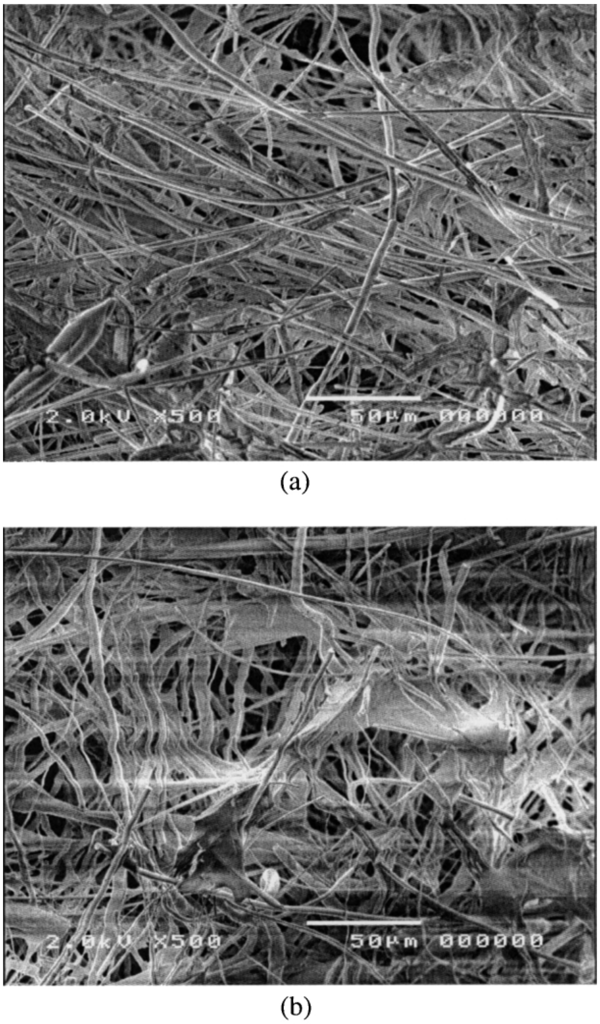

Fig. 12. Microstructure of sintered fibre product with Bindzil 50/80 (a) (4 g SiO_2); (b) (11 g $SiO_2 = 880 m^2$). Optimum retention of binder.

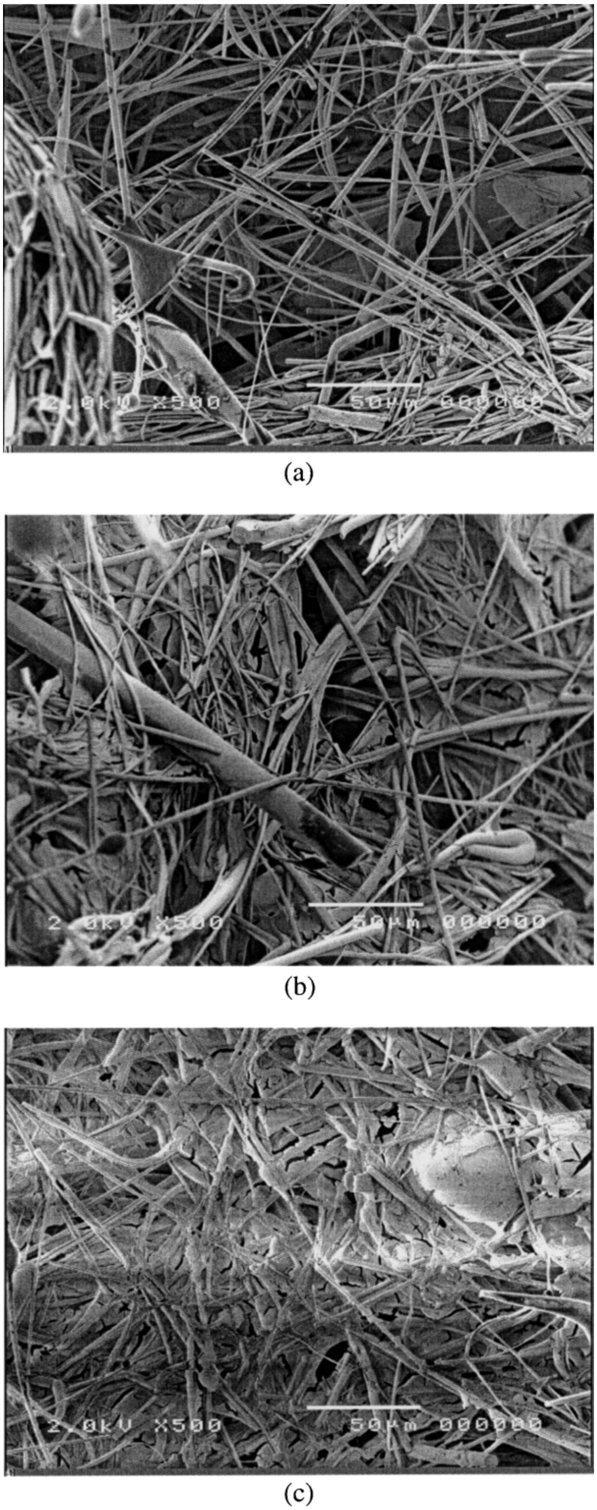

Fig. 13. Microstructure of sintered fibre product with Bindzil 40/220 (4 g $SiO_2 = 880$ m^2). (a) 70% retention of silica; (b) optimum retention of binder; (c) high retention of silica, but excess of starch added.

presence of cracks in the gel did not influence the compressive strength values, but it cannot be ruled out that the properties of the gel might have an effect on the long-term properties (resistance to thermal cycling etc.).

Some results indicate that the amount of starch had an effect on the appearance of the silica gel, and as an example of this Fig. 13a–c can be studied. In this case the amount of silica added was the same (4 g), but the amounts of starch added varied, which meant that the retention would be different. In the sample shown in Fig. 13a too small an amount of starch was added, whereas in the sample shown in Fig. 13c an excess of starch was added. Sample 13a was very brittle (σ_{10} low) and in the micrographs hardly any silica could be detected between the fibres although silica was retained (70% retention). The silica holding the fibres together can be observed in the sample shown in Fig. 13b, which was prepared in the optimum retention regime. The sample prepared with an excess of silica has a different appearance (Fig. 13c), although the amount of silica was quite the same as in the sample shown in Fig. 13b. In Fig. 13c the structure of the gel looks much thicker than that in Fig. 13b. The gel is not only between fibres, but it surrounds the fibres as well. These results indicate that the amount of starch influenced the formation of the silica gel. However, this must be confirmed by further microstructural investigations.

4. Discussion

This study has focussed on two different functions of colloidal silica sols in the application as refractory fibre binders, i.e. their *flocculation behaviour* and their effect on the *mechanical properties* of the shaped, dried or fired products. The effect of the silica sols on the high-temperature properties or on thermal shock behaviour has not been within the scope of this study, but these aspects are of course very important.

When producing this kind of fibrous material, the goal is to add a minimum amount of binder. This can be achieved if the binder is located in the right place, i.e. in the contact points between the fibres. The minimum amount of silica to use has not been determined in this study, but the study has shown that 4 wt.% silica (based on fibre weight) can be used for all the sols. For the sol with the highest specific surface area (360 m^2/g), an even smaller amount of silica can be used, such as 2.44 wt.%. This amount of silica gave good flocculation and acceptable mechanical properties of the products. However, even with this relatively small amount of silica added, the micrographs show that silica was found not only in the contact points between the fibres, but also in the spaces between the fibres. This indicates that it might be possible to further decrease the amount of silica.

4.1. Flocculation behaviour

The flocculation behaviour of the system is critical for the preparation of the fibrous products. It is known[21] that the efficiency of a microparticle system based on starch depends on the charge densities of the components and on the size and structure of the starch and the colloidal silica. In this study, it has been shown that there are many parameters affecting the flocculation behaviour, such as the order of the additions, the type and amount of silica and starch added and the ionic strength of the system. Especially the ionic strength turned out to be a parameter with a significant influence on the flocculation behaviour. To be able to control the flocculation process, it is, therefore, very important to have control of the water in the system, especially in closed systems, in which the process water is reused.

All four sols, with particle sizes from 9 to about 40 nm, showed excellent flocculation behaviour. The retention was highest for the sol with the lowest specific surface area (Bindzil 50/80) and decreased slightly with an increase in specific surface area of the sol. More studies are needed to confirm if there exists an optimal particle size of the colloidal silica, which would give the best flocculation result. It can be mentioned that Andersson and Lindgren[21] have shown that there exists a critical minimum size of the sol particles at around 3–5 nm to get a proper flocculation of cellulosic fibres. Good flocculation was not obtained below this size. The amount of starch required to reach optimum retention in our study was related to the total surface area of the silica added, since all the colloidal sols used had the same surface charge behaviour. One advantage of using a sol with a low specific surface area (as Bindzil 50/80) is that only a very small amount of starch needs to be added to reach optimum retention. In many applications, there is a desire to reduce the amount of organic binder, both for economic and for environmental reasons, and it would be attractive if the burnout of organic materials could be avoided.

All experiments have been performed using the same type of starch, but similar results would be obtained with other types of cationic starches. However, the optimal amount of starch to use is strongly correlated to the charge density (D.S. value) of the starch molecule.

4.2. Effect on mechanical properties

The results show that it might be difficult to rate different silica binders, especially when considering how they affect the mechanical properties of the final product. The reason for this is that there are several different factors that influence the result. As an example, it can be mentioned that this study has shown that the compressive strength very much depends on the density of the fibre bodies, and it has also been shown that the density is determined mainly by the amount of starch added to the fibre products. This was true for both the green products and the sintered ones. However, for the green samples the amount of starch in the sample was also very important for the compressive strength obtained. The silica content of the sintered samples was not so important as the density.

Therefore, if the properties of the true silica binder are to be evaluated, the fibre products should have the same density and contain the same amount of silica (i.e. have the same surface area) and the same amount of organic binder. High density means that there will be more contact points between the fibres and a high content of binder based on the total volume of the fibre cake. It should be noted that, although the density is such an important factor, it is hardly ever presented when mechanical data on these kinds of fibrous products are published.

One interesting observation was that the fibre products prepared with the low-surface silica sol — Bindzil 50/80 — got higher densities than those obtained with the other sols. One explanation to this might be that Bindzil 50/80 contains particles with a wide size distribution, which enhances the packing of the sol particles. This may lead to a denser gel compared with what was obtained using the other sols. This corresponds well with the nearly crack-free binder phase observed in the sintered fibre products with Bindzil 50/80. Another possible advantage of using Bindzil 50/80 with low specific surface area (80 m^2/g) might be that the low content of starch required means that the fibre bodies will have a nearly constant compressive strength, irrespective of the firing temperature.

One way of getting the same density of the products would be to press all fibre cakes to a fixed height during vacuum forming. On the other hand, it is interesting to note that fibre slurries, prepared in exactly the same manner, gave different fibre packing during the vacuum forming stage, when the amount of starch and the type of sol (especially with Bindzil 50/80) were changed. It should be emphasised that the control of the density might be an important task for other reasons, as the density (i.e. the porosity) affects the thermal conductivity of the products. This aspect of the density variation has not been considered in this study.

The results have shown that maximum in compressive strength of the fibre products was obtained outside the regime of optimum flocculation, i.e. it was reached when an excess of starch had been added. Since the retention of silica and starch is not optimal in this region, it is often not interesting to work under these conditions. When choosing a system to work with, both the flocculation behavior (i.e. the retention) *and* the mechanical properties must be taken into consideration.

Finally, the results obtained using Bindzil 50/80, i.e. the sol with the largest particles and lowest specific surface area, differed in many ways from the results obtained with the other sols. Bindzil 50/80, for instance, gave the highest retention of silica, the highest density of the fibre cakes and the binder phase with the fewest cracks. The reason for this behaviour must be further examined. It would, for instance, be interesting to see how the different sols affect the floc sizes and floc strengths.

This study has shown that this three-component system (ceramic fibre/silica sol/starch) is a very complex system and more research is needed to obtain a better understanding of the system.

5. Conclusion

A deeper understanding of the effects of the varied parameters on the ceramic fibre–silica sol–starch system has been obtained through this study. It has been shown that the way in which the fibrous materials are fabricated is very critical for the retention of silica and starch. Parameters, which affect the retention (and the flocculation behaviour), are — besides the type of silica and starch used — also the type of process water (ionic strength) used and the order in which the different components are added. In the optimum retention regime the effluent is clear (turbidity <5 NTU) and $>94\%$ of the added starch and silica is retained, which leads to fibre bodies with a very homogeneous distribution of the binder. At optimum retention a constant ratio between the starch content and the total surface area of the added silica is obtained for silica sols with the same surface charge, regardless of their particle size (sols with the diameters of 9–40 nm were evaluated). At low ionic strength more starch is needed to obtain the desired flocculation behaviour.

In general the strength of the green samples was higher than the strength of the sintered samples (1000°C), as the starch is a very effective binder. The compressive strength of the fibrous products very much depended on the density of the fibrous material. The density increased with an increased amount of starch, which led to higher compressive strength. This was true both for the green and the sintered samples. This indicates that the starch molecules acted as a lubricant, enhancing the rearrangement of the fibres and affecting the packing of the fibres (and the density of the fibrous material). It can be concluded that the highest compressive strength is **not** obtained under the same conditions as when optimum retention is obtained. When considering the flocculation behaviour and the mechanical properties, the silica sol with the intermediate specific surface area, Bindzil 40/220 (220 m^2/g) has very good properties. However, in those cases when it is important to reduce the organic content to a minimum, the silica sol with a low specific surface area should be chosen (as Bindzil 50/80 with 80 m^2/g). This sol also gave the highest retention of silica and a nearly crack-free binder phase after sintering.

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